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Exploring the Degradation of Malachite Green Using Fenton and Photo-Fenton Processes

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Abstract

The degradation of Malachite green (MG) dye was studied using Fenton and Photo-Fenton processes. Batch experiment was conducted for the effect of pH at the range of (3–12), initial concentration at 50–250mg/L, effect of catalyst dosage of 0.2-1.0g, contact time (10–60min) and temperature (303–318) were evaluated. For each experiment, the reactor was loaded with 30mL of 50mg/L of MG aqueous solution and 20ml of 50mmol of hydrogen peroxide to which 0.5g of the ferrous catalyst was added. As investigated, the degradation capacity of Fenton and Photo Fenton was favoured by an increase in dosage, concentration, and contact time. While degradation decreases with increase in temperature and pH. The optimum pH for the degradation of MG was found to be 3. The experimental data of MG fitted better into Freundlich equation indicating multilayer degradation. Also the Kinetic data fitted more into pseudo second order than in pseudo first order equation for both Fenton and photo Fenton suggesting chemisorptions as the rate limiting step. The negative value of enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy (ΔG) indicating that the degradation of Malachite Green was exothermic and spontaneous, meaning that physisorption dominate chemisorptions. Overall, Fenton and Photo Fenton as investigated in the present study; it is an evident

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that Photo-Fenton has higher potency for degradation of Malachite green than that of Fenton.

Keywords: Degradation, Malachite green, Fenton, Photo-Fenton

INTRODUCTION

Due to the rapid advancement of technology, industry, and urbanization, large amounts of toxins that threaten microorganisms, animals, and plant life even at low concentrations have been released into the aquatic environment (Baig *et al.*, 2019). Among these pollutants, synthetic dyes, predominantly used in the textile industry for dyeing and printing processes, are particularly concerning (Mittal *et al.*, 2020).

Fenton and Photo-Fenton processes are innovative methods for degrading organic pollutants (Bello *et al.*, 2019). These methods involve the reaction of ferrous ions with hydrogen peroxide to produce hydroxyl radicals (•OH), which are highly reactive and strong oxidants with an oxidation potential of 2.8 eV (Krystynik, 2021). These radicals can oxidize organic contaminants into harmless H_2O and CO_2, as described by the Haber–Weiss mechanism (Ren *et al.*, 2020). The Fenton process has significant advantages, including reduced sludge generation and the high efficiency of H_2O_2. However, since the reaction rate in the classical Fenton process decreases over time, external energy, such as ultraviolet (UV) radiation, is required to accelerate the degradation in the Photo-Fenton process. UV radiation enhances the decomposition of H_2O_2 into hydroxyl radicals and converts ferrous ions to ferric ions, thereby increasing the degradation rate of contaminants like methyl green (MG) through faster reaction pathways.

METHODS

Reagent preparation

Preparation of 50 mmol of H_2O_2 from 50% stock

3.1 ml of 50% concentration H_2O_2 was measured and added to 500 ml of water. This mixture was then transferred into a 1000 ml volumetric flask and filled to the mark with distilled water. The solution was then shaken to ensure it was homogeneous.

Preparation of 0.1M of HCl solution

To prepare a 0.1 M HCl solution, 8.60 cm^3 of HCl acid was carefully measured and added to 100 cm^3 of water. This mixture was then transferred into a 1000 ml volumetric flask, filled to the mark with distilled water, and shaken to ensure homogeneity.

Preparation of 0.1M of NaOH solution

A quantity of 4.08 g of NaOH was weighed into a beaker and dissolved in 100 ml of water. This solution was then transferred into a 1000 ml volumetric flask, filled to the mark with distilled water, and shaken to ensure homogeneity.

Fenton and Photo Fenton experiment

The decolorization of MG dye was conducted in a batch process. The dye solution was prepared in distilled water, and the Fenton degradation tests were performed in a 500 mL glass beaker under various conditions. These conditions included a Fenton dosage of 50 mmol H_2O_2, 0.5 g ferric oxide, and different parameters such as pH values ranging from 3 to 12, temperatures from 303 to 318 K, contact times from 10 to 60 minutes, initial MG concentrations from 50 to 250 mg/L, and catalyst dosages from 0.2 to 1.0 g. For each experiment, the reactor was loaded with 30 mL of 50 mg/L MG solution and 20 mL of 50 mmol H_2O_2, to which 0.5 g of ferrous catalyst was added. The pH was adjusted with 0.1 M HCl and 0.1 M NaOH, and the mixture was stirred for 60 minutes.

The UV-Vis spectrum of each MG solution was determined using a Cecil 7200 spectrophotometer with a 1 cm quartz cuvette. The spectrum was scanned from 200 to 800 nm, and a calibration curve was created using the dye's maximum absorbance wavelength. MG degradation was calculated using Eq. (1).

$$\% = \frac{(A_o - A_t)}{A_o} \times 100\% \qquad (1)$$

where A_0 and A_t are the absorbance of MG after treatment time t in minutes, at corresponding t_{ax} respectively.

The photo-Fenton reaction was conducted under the same parameters and conditions as the Fenton reaction in a UV reactor. This reactor was equipped with a LED bulb (model AP-2916) with the following specifications: 20 watts of power, a voltage range of 90-265 volts, an operating temperature range of 20-80°C, a frequency range of 50-60 Hz, a color temperature between 6800-7300K, and a humidity range of 20-80%.

Effect of contact time

In this study, the degradation rate of MG was evaluated using various kinetic models, including pseudo-first-order and pseudo-second-order models, at different time intervals (10 - 60 minutes). The experiments were conducted with a catalyst dosage of 0.5 g, 30 mL of a 50 mg/L MG solution, 20 mL of a 50 mmol H_2O_2 solution, and at room temperature.

Effect of Catalyst dosage

The impact of catalyst dosage on MG degradation was investigated by varying the dosage of ferric oxide (0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g) with a 60-minute shaking time. The experiments used 20 mL of a 50 mmol H_2O_2 solution and 30 mL of a 50 mg/L MG solution.

Effect of temperature

Degradation of MG was studied at various temperatures (25, 30, 35, 40, and 45°C) to determine different thermodynamic models. The experiments were conducted using 20 mL of a 50 mmol H_2O_2 solution, 20 mL of a 50 mg/L MG solution, and 0.5 g of ferric oxide as the catalyst dosage, with a shaking time of 60 minutes.

Effect of Initial concentration of MG

The degradation of MG was investigated at various initial concentrations (50-250 mg/L). The experiments were conducted using 20 mL of a 50 mmol H_2O_2 solution, 30 mL of an MG solution with a concentration of 50 mg/L, and 0.5 g of ferric oxide as the catalyst dosage, with a shaking time of 60 minutes.

Effect of pH

The effect of pH on MG degradation was investigated by adjusting the pH to 3, 5, 7, 9, and 12. The experiments used 0.5 g of ferric oxide as the catalyst, 30 mL of a 50 mg/L MG solution, and 20 mL of a 50 mmol H_2O_2 solution, conducted at room temperature with a shaking time of 60 minutes.

RESULTS AND DISCUSSION

Batch Degradation Parameters

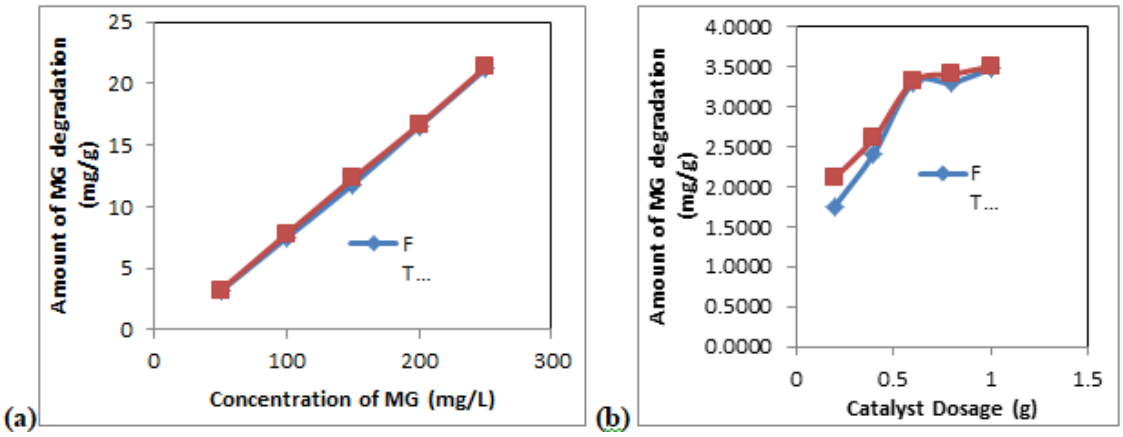


FIGURE 1: (a) Effect of Initial Concentration on Degradation of MG (b) Catalyst Dosage on Degradation of Malachite Green

Effect of Initial Concentration of MG Dye

The results shown in Figure 1a illustrate the effect of initial MG concentration on its degradation using Fenton and photo-Fenton processes. For the Fenton process, it was observed that as the initial concentration of MG increased from 50 to 250 mg/L, the percentage removal decreased from 84.7% to 63.1%. Similarly, for the photo-Fenton process, the percentage removal decreased from 85.3% to 64.3%. These results indicate that as the initial concentration of MG increases, its degradation decreases. This reduction in degradation efficiency is attributed to the limitation of ferrous ions available to react with hydrogen peroxide to produce hydroxyl radicals (•OH), which are responsible for MG degradation. However, the photo-Fenton process enhances the rate of degradation by increasing the decomposition of hydrogen peroxide to produce more hydroxyl radicals (Goi & Trapido, 2002) and converting ferrous ions to ferric ions, thereby increasing the rate of MG degradation, as indicated by the percentage removal.

Effect of Catalyst Dosage

The effect of catalyst dosage on MG degradation using Fenton and photo-Fenton processes is presented in Figure 1b, the Fenton process; it was observed that as the catalyst

dosage increased from 0.2 g to 1.0 g, the percentage removal increased from 35.2% to 69.6%. Similarly, for the photo-Fenton process, the percentage removal increased from 42.2% to 70.1%. This increase in MG degradation with higher catalyst dosage is related to the increased number of active sites and ferrous ions available to react with hydrogen peroxide to produce hydroxyl radicals, which are responsible for MG degradation. Additionally, that the photo-Fenton process further enhances the degradation rate by increasing the production of hydroxyl radicals (Carbajo *et al.*, 2021) and converting ferrous ions to ferric ions, leading to a higher rate of MG degradation as indicated by the percentage removal. The reaction can be represented in Equation 2 below

$$Fe^{IIsites} + \bullet OH \longrightarrow \equiv Fe^{IIIsites} + OH^{-} \quad (2)$$

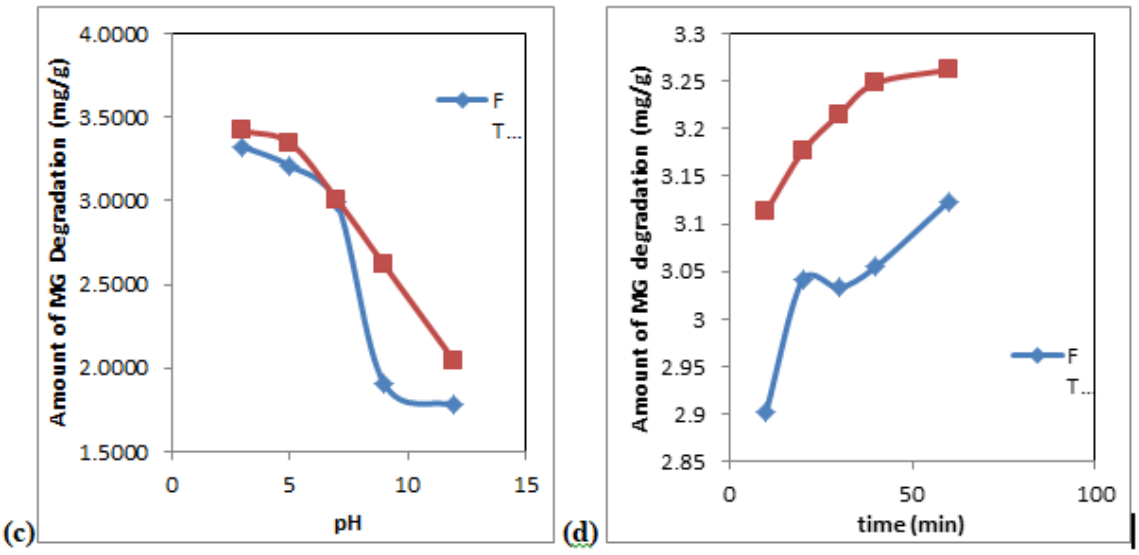


FIGURE 2: (c) Effect of pH on Degradation of MG (d) Effect of Contact Time on Degradation of Malachite Green

Effect of pH

The impact of pH on MG degradation using Fenton and photo-Fenton processes is illustrated in Figure 2c. For the Fenton process, it was observed that as the pH increased from 3 to 12, the percentage removal decreased from 66.5% to 35.6%. Similarly, for the photo-Fenton process, the percentage removal decreased from 68.4% to 40.8%. This indicates that as the pH increases, the degradation rate decreases for both processes. The results in Figure 4 suggest that the optimal pH for MG removal using both Fenton and photo-Fenton processes is pH 3. This implies that hydroxyl radical (•OH) generation is

more effective in acidic conditions. At higher pH levels, ferrous and ferric hydroxides are formed, inhibiting the reaction between Fe^{2+} and H_2O_2 and reducing hydroxyl radical production. Additionally, H_2O_2 is unstable in alkaline solutions and decomposes into H_2O and O_2 as shown in Equation (3) (Liu *et al.*, 2016). At very low pH levels (below pH 3), excessive H^+ reacts with H_2O_2 to produce H_3O_2, which is stable and does not react with iron (II) to form hydroxyl radicals as shown in Equation (4) (Patel *et al.*, 2020; Chen *et al.*, 2019). The results in Figure 2c also show that the photo-Fenton process increases the degradation rate more than the Fenton process, as indicated by their respective percentage removals.

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \quad (3)$$

$$Fe^{2+} + H_2O_2 + H^+ \longrightarrow H_3O_2 \quad (4)$$

Effect of Contact Time

The effect of contact time on MG degradation using Fenton and photo-Fenton processes is presented in Figure 2d. For the Fenton process, it was observed that as the contact time increased from 10 to 60 minutes, the percentage removal increased from 58.1% to 61.1%. Similarly, for the photo-Fenton process, the percentage removal increased from 62.5% to 65.3%. These results indicate that increasing the contact time enhances the degradation rate of MG for both processes. The optimal contact time for MG degradation using Fenton and photo-Fenton processes is 60 minutes, as shown in Figure 2d. Based on the percentage removal, it can be concluded that the photo-Fenton process is more effective than the Fenton process.

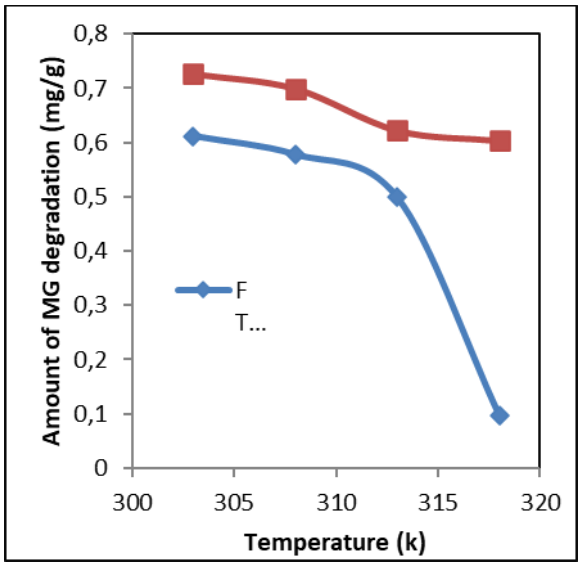
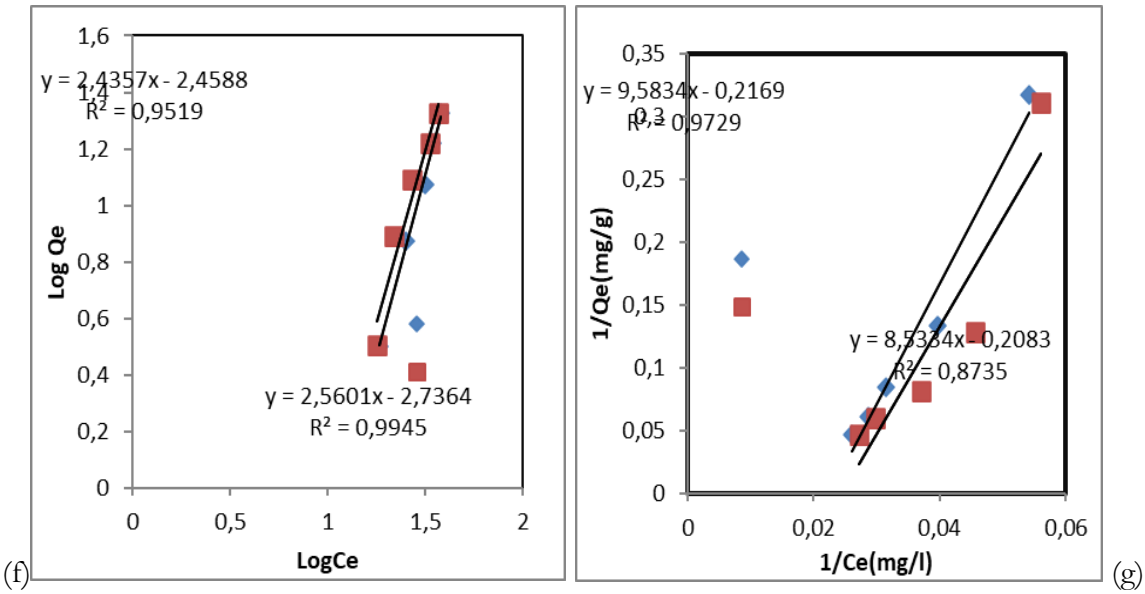


Figure 3. Effect of Degradation of MG against temperature

Effect of Temperature

The impact of temperature on MG degradation using Fenton and photo-Fenton processes is presented in Figure 3. For the Fenton process, it was observed that as the temperature increased from 303K to 318K, the percentage removal decreased from 62.3% to 53%. Similarly, for the photo-Fenton process, the percentage removal decreased from 64.5% to 62.1%. These results indicate that the degradation rate of MG decreases with increasing temperature for both processes. The optimal temperature for MG degradation using both Fenton and photo-Fenton processes is 303K. Additionally, the results show that the photo-Fenton process enhances the degradation rate more than the Fenton process, as evidenced by their respective percentage removals.

Isotherm Model for the Degradation of Malachite Green



(f) (g)

Figure 4. (f) Freundlich Isotherm Plot for the Degradation MG (g) Langmuir Isotherm for the Degradation of MG

Table 1. Freundlich and Langmuir Parameters for Fenton and Photo Fenton process

Freundlich isotherm				Langmuir isotherm			
	nf	Kf	R^2	Qm	B	R_l	R^2
Fenton	0.391	0.002	0.995	-4.610	-0.023	0.021	0.973
Photo Fenton	0.411	0.003	0.952	-4.801	-0.024	0.021	0.874

Degradation Isotherm

To study the degradation isotherms of MG for both Fenton and photo-Fenton processes, the Freundlich and Langmuir equations were utilized. The results, presented in Figure 4f and 4g, and Table 1 above, indicates that for the Fenton process, the degradation of MG is better described by the Langmuir equation, which has a higher correlation coefficient (R^2 = 0.973) compared to the Freundlich equation (R^2 = 0.952). This suggests that the Langmuir model more accurately represents the degradation process. However, the close correlation coefficient of the Freundlich equation indicates that it also provides a reasonable fit for the data.

In contrast, for the photo-Fenton process, the degradation of MG fits the Freundlich equation more effectively, as shown in Figure Figure 4f and 4g, and Table 1 above, with a correlation coefficient of $R^2 = 0.995$. This higher value indicates that the Freundlich model, which represents multilayer adsorption, better describes the degradation process for photo-Fenton. The Freundlich isotherm's higher correlation coefficient compared to the Langmuir equation supports the conclusion that the degradation of MG in the photo-Fenton process follows a multilayer adsorption mechanism.

Kinetic Model for the Degradation of MG

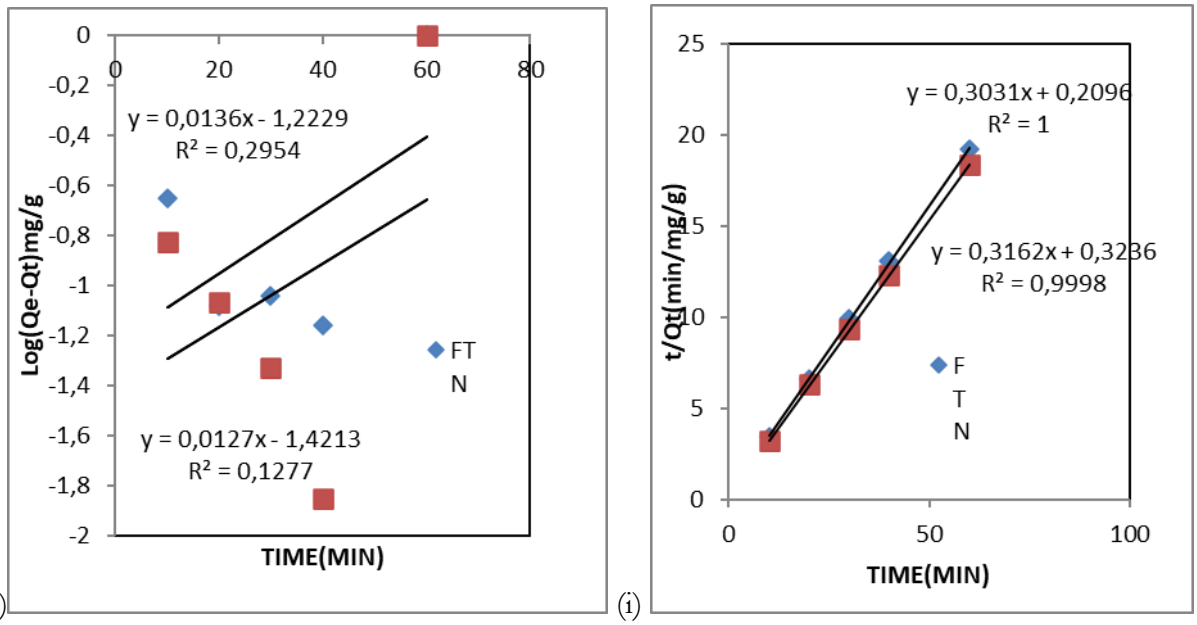


Figure 5: (h) Pseudo first order kinetic model (i) Pseudo Second Order Kinetic Model

Table 2. Kinetic Parameters for the degradation of MG using Fenton and photo Fenton

1^{ST} ORDER	K_1	Qe	R^2	2nd ORDER	K_2	Qe	R^2	H
Fenton	-0.0313	0.060	0.295		3.090	3.163	0.324	30.902
Photo Fenton	-0.029	0.038	0.128		0.438	3.299	1.000	4.771

Kinetic Model

To analyze the kinetic models of MG degradation for both Fenton and photo-Fenton processes, pseudo-first-order and pseudo-second-order equations were utilized. These models describe the reaction kinetics over time. The results, detailed in Figure 5h and 5i, and Table 2 above, shows that both Fenton and photo-Fenton processes are better represented by the pseudo-second-order equation. This is supported by the Van't Hoff plot of t/Q versus t, which yields a straight line, confirming the applicability of the pseudo-second-order model. This linearity suggests that chemisorption is the rate-limiting step in the degradation process (Sebeia *et al.*, 2019).

Table 2 further demonstrates that the pseudo-second-order model provides higher correlation coefficients for both Fenton and photo-Fenton processes (R^2 = 0.324 and 1.000, respectively) compared to the pseudo-first-order model (R^2 = 0.295 and 0.128, respectively). The better fit of the pseudo-second-order model, along with the linear Van't Hoff plot, indicates that this model more accurately describes the degradation kinetics of MG for both processes.

Thermodynamic Parameters for the Degradation of MG

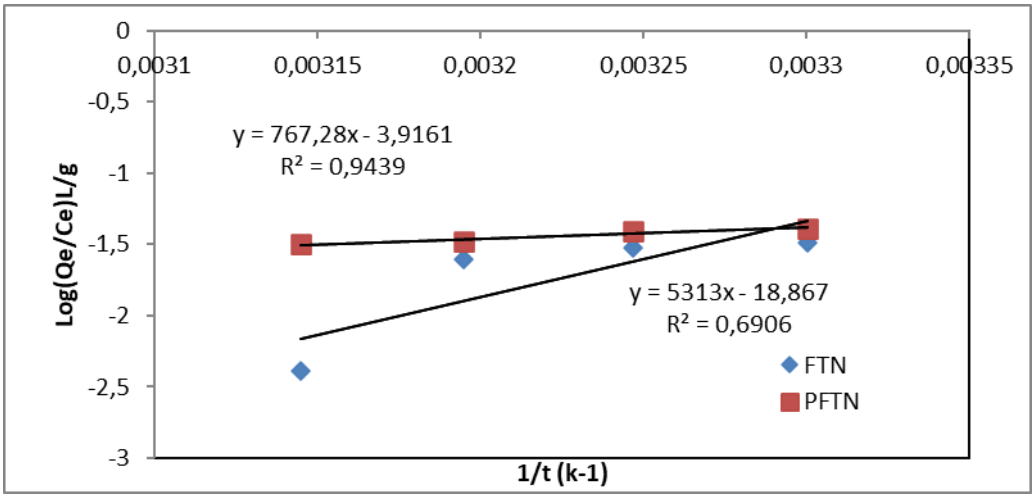


Figure 6. Van't Hoff plot of degradation Thermodynamic for degrading MG using Fenton and photo Fenton processes

Table.3. Thermodynamic Parameters for the Degradation of MG using Fenton and Photo Fenton

Thermodynamic	Δs(kJ mol−1 K−1)	ΔG (Kj/mol)	ΔH (Kj/mol)	R^2
Fenton	-361. 259	-196. 272	-101. 728	0.691
Photo-Fenton	-74. 982	-283. 3087	-14.691	0.944

Thermodynamics parameter

The thermodynamic parameters of the degradation processes are essential for evaluating the temperature dependence of these reactions (Thaligari *et al.*, 2016). To assess the spontaneity and feasibility of the degradation processes, Gibbs free energy change (ΔG^0), change in enthalpy (ΔH^0), change in entropy (ΔS^0) were analyzed for both Fenton and photo-Fenton processes. From the results shown in Figure 6 and Table 3 above, it was observed that for the Fenton process, the enthalpy (ΔH^0) were found to be -101.728 KJ/mol. This negative value indicates that the degradation of MG is exothermic. The Change in entropy (ΔS^0) were found to be -361.259KJ/mol/K, and its negative value suggests that the rate of degradation is relatively slow. The Gibbs free energy change (ΔG^0), were found to be -196.272 KJ/mol, which indicates that degradation process is spontaneous.

For the photo-Fenton process, enthalpy (ΔH^0) were found to be -14.691KJ/mol, also reflecting an exothermic reaction. The Change in entropy (ΔS^0) were found to be -74.982KJ/mol/K, indicating a slow degradation rate. The Gibbs free energy change (ΔG^0), were found to be -283.309KJ/mol, suggesting that the degradation process is spontaneous. The exothermic nature and spontaneity of both processes imply that physisorption dominates over chemisorption in these degradation reactions (Ji *et al.*, 2021).

CONCLUSION

The removal efficiency of MG for both the Fenton and photo-Fenton oxidation processes was evaluated under various experimental parameters. The results indicated that the degradation capacity for both methods improved with increased catalyst dosage. This is due to a higher number of active sites and an increased amount of ferrous ions reacting with hydrogen peroxide to generate hydroxyl radicals (•OH), which are responsible for MG

degradation. The degradation was also influenced by the initial concentration of MG and contact time. Conversely, an increase in temperature led to a decrease in percentage removal.

The optimal pH for MG degradation was found to be 3. This is because the activity of the Fenton reagent diminishes at higher pH levels, likely due to the formation of relatively inactive ferryl ions (FeO_2^+) (Wang *et al.*, 2019). Additionally, H_2O_2 is unstable at higher pH (alkaline solutions) and decomposes into H_2O and O_2 (Liu *et al.*, 2016). High-valent iron species generated in alkaline solutions are less reactive compared to hydroxyl radicals (•OH). The experimental data fit the Freundlich isotherm better than the Langmuir isotherm, indicating multilayer adsorption. Kinetic data were more consistent with the pseudo-second-order model than the pseudo-first-order model, suggesting that chemisorption is the rate-limiting step due to the higher correlation coefficient of the pseudo-second-order model.

The negative values for enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy (ΔG) indicate that the degradation of MG is exothermic and spontaneous, with physisorption dominating over chemisorption. Compared to the Fenton process, the composite photo-Fenton process demonstrated a higher percentage of MG degradation, highlighting its superior effectiveness.

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